

Analytical, Nutritional and Clinical Methods Section

# Application of a liquid chromatographic method for the determination of phenolic compounds and furans in fortified wines

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## Abstract

Fortified wines which suffer extended periods of wood ageing develop characteristics which in many cases define the product. An important component of this style is contributed by the specific phenolic compounds and furans which are either extracted from the wood or formed during the barrel ageing process. An HPLC method is presented here for the determination of phenolic compounds and furans in wood aged fortified wines. The method employed involved direct injection with no sample pre-treatment, separation on a RP C<sub>18</sub> column in a single run and detection with a diode array detector. In this way up to 28 compounds from various phenolic groups (hydroxybenzoic acids, hydroxycinnamic acids, phenolic aldehydes, coumarins, flavan-3-ols, flavonol aglycones) and other compounds involved in browning reactions in food systems (furans and pyranones) could be separated and determined. Of these, 10 phenolic compounds, gallic acid, protocatechuic acid, *p*-coumaric acid, caffeic acid, chlorogenic acid, ellagic acid, vanillic acid, syringic acid, *p*-hydroxybenzaldehyde, myricetin, and two furans; furfural, 5-hydroxymethyl-2-furaldehyde, were determined in fortified and similar wood aged wines. Three other compounds, a chlorogenic acid isomer, vanillin and resorcinol, were also tentatively identified in these wine types. © 1998 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Fortified wines are fermented or partly fermented wines which have been supplemented with distilled spirit of grape origin. These include products as diverse as port and madeira (Portugal), sherry (Spain), vins doux naturels (France) and various other products from Australia, South Africa or USA, which may or may not be produced to resemble the European products listed. Many fortified wines are produced in such a way that their composition enables them to withstand considerable ageing either in bottle or in wooden cask, the characteristics developed during this ageing being perceived as essential to their style. Tokay wines, which originate from Hungary, range from dry to sweet and are characterised by a large amount of extract, displaying characteristic flavour and aroma (Farkaš, 1988). Tokay Aszú wines, which are the best known of these wines, are aged for at least 4 years in wooden cask, their characteristics lead them to be considered in the same category as wood-aged fortified wines and for this reason they are included in this study.

Phenolic compounds are the major substrates for the consumption of oxygen in wine, participating in many oxidation-reduction reactions (Singleton, 1987; Fabre, 1994). These compounds contribute directly or indirectly to colour (Ribéreau-Gayon, 1982), astringency and bitterness (Arnold and Noble, 1978; Robichaud and Noble, 1990), aroma (Chatonnet, 1993), and they are also involved in browning reactions in both grapes and wines (Macheix et al., 1991). Ageing of wines in wooden barrels can increase the pool of oxidisable phenolic substances through extraction of these compounds from the wood (Puech, 1987; Piergiovanni et al., 1988).

Browning reactions are known to occur during processing and storage affecting the flavour, appearance, and nutritive value of a product. Furans are a group of compounds that are formed during nonenzymatic browning reactions, such as caramelization, which involves the degradation of sugars, and the maillard reaction, involving amadori rearrangement compounds (Eskin, 1990). Furans have been found in both tawny ports (Williams et al., 1983) and in sherry (Shimizu and Watanabe, 1979), contributing to the brown colour of these wood-aged wines.

Work published in recent years have shown high-performance liquid chromatography to be the method

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of choice in the analysis of phenolic compounds present in wines. Due to the complex nature of these beverages, samples must be pretreated before analysis. Pretreatment methods which are mainly based on liquid–liquid extraction (Salagoity-Auguste and Bertrand, 1984; Estrella et al., 1986; Puech, 1987; Revilla et al., 1988; Woodring et al., 1990; Laszlavik et al., 1995) and solid phase extraction (Lunte et al., 1988; Oszmianski et al., 1988; Cartoni et al., 1991), can result in errors in estimating the true quantities present. The search for more accurate quantification methods have led researchers to develop direct injection techniques using diode array detection (Roggero et al., 1990; Lamuela-Raventos and Waterhouse, 1994; Goldberg et al., 1996), multi-wavelength detection combined with spectrofluorimetry (Moutounet et al., 1989), or electrochemical detection (Achilli et al., 1993). Although there is a great deal of information in the literature on phenolic compounds in table wines (Table 1), there is little on fortified wines. Of that which is reported most have focused on sherry (Estrella et al., 1986; Revilla et al., 1988; Guillén et al., 1993; Barón et al., 1997), although anthocyanins have been quantified in young port wines (Bakker and Timberlake, 1985). Apart from the lack of information on phenolic compounds in fortified wines, very few HPLC methods are concerned with the combined analysis of phenolic compounds and furans. Moutounet et al. (1989) used a direct injection method with multi-wavelength detection combined with spectrofluorimetry to determine these compounds in Chardonnay wine, while Estrella et al. (1986) using ultraviolet detection, analysed ethyl ether extracts of sherry wines. Combined HPLC analysis of both phenolic compounds and furans have also been developed for other biological substrates such as for maple products (Kermasha et al., 1995a) and apple juice (Kermasha et al., 1995b).

The objective of this study was to develop a HPLC technique suitable for analysing both phenolic compounds and furans in a variety of fortified wines. Samples were injected directly into the HPLC, without the need for sample pre-treatment, with phenolic compounds and furans identified using a diode array detector. The identification and quantification of these compounds are reported in Tawny port, Madeira, Amontillado sherry, Banguls and in Tokay Aszú wines.

## 2. Materials and methods

### 2.1. Wines

Wines analysed were tawny ports consisting of a Colheita 1990 and Colheita 1960 (Port wine with date of harvest), a 10 years old and a 30 years old Aged Tawny port (Port with indication of age). Other wines included a solera medium Amontillado sherry, a 10 years old

Verdelho madeira, a Banyuls Rimage 1989, a Banyuls 1977 (tawny type), a Tokay Aszú 5 puttonyos 1983 and a Tokay Aszú 4 puttonyos 1988.

### 2.2. High performance liquid chromatography system

All samples were analysed by direct injection on a Beckman System Gold<sup>™</sup> High Performance Liquid Chromatography system (Beckman Instruments, Inc., Fullerton, CA, USA) equipped with a Beckman Model 168 Diode Array detector and Beckman model 502 autosampler. Beckman system Gold<sup>™</sup> HPLC software version 6.01 was used for data acquisition and analysis. Phenolic compounds and furans were separated on a 250 mm×4.6 mm Spherisorb S5 ODS2 column (Phase separations Ltd, Clywd, UK) which was controlled at 25°C±1 using a temperature controlled Croco-Cil No. 726 Oven.

### 2.3. Chromatographic conditions

HPLC Separation conditions: Solvent A, water-formic acid (98:2); Solvent B, 700 ml of methanol containing 2% formic acid with 300 ml of Solvent A. Gradient elution program was: 3 min at 0% B, to 10% B in 7 min, to 40% B in 50 min, to 60% B in 20 min, to 100% B in 25 min, 15 min at 100% B, return to initial conditions in 20 min; flow rate, 1.0 ml min<sup>-1</sup>; injection volume, 20 µl. Phenolic compounds and furans were detected at 280 nm and 320 nm.

### 2.4. Peak characterisation and quantification

Phenolic compounds and furans were characterised by their UV spectra which were recorded from 190 nm to 402 nm (2 nm steps). Peaks were identified by superimposing the spectra of each peak with the corresponding spectra of standard compounds, by the comparison of their retention times and in some cases by spiking the wine with pure standards. Quantification was based on peak areas as determined by Beckman System Gold<sup>™</sup> HPLC software version 6.01 using external standards. Linear calibration curves for standards (peak area vs concentration) were constructed with  $R^2$  exceeding 0.999.

### 2.5. Standards for peak characterisation

Gallic acid, *p*-hydroxybenzoic acid, protocatechuic acid, gentisic acid, *p*-coumaric acid, caffeic acid, ferulic acid, ellagic acid, vanillic acid, syringic acid, vanillin, *p*-hydroxybenzaldehyde, syringaldehyde, (+)-catechin, (–)-epicatechin, esculin, esculetin, scopoletin, resorcinol, myricetin, quercetin, furfural, 5-methylfurfural, 5-hydroxymethyl-2-furaldehyde (HMF), maltol were purchased from Sigma. Chlorogenic acid and Salicylic acid (Merck), coniferaldehyde (Aldrich).

Table 1  
Literature review on the presence of phenolic compounds and furans in fortified wines and table wines

References	Type of wine	Compounds identified
	<i>Fortified wines</i>	
Bakker and Timberlake (1985)	Young port wine	Delphinidin-3-glucoside, petunidin-3-glucoside, cyanidin-3-glucoside, malvidin-3-glucoside, peonidin-3-glucoside, malvidin-3-glucoside-acetate, malvidin-3-glucoside- <i>p</i> -coumarate, peonidin-3-glucoside- <i>p</i> -coumarate
Estrella et al. (1986)	Fino, oloroso and amontillado Sherrys	Gallic, protocatechuic, vanillic, syringic, gentisic, caffeic, <i>p</i> -hydroxybenzoic, <i>p</i> -hydroxycinnamic and ferulic acids, and vanillin, esculetin, <i>p</i> -hydroxybenzaldehyde, 3,4-di-hydroxybenzaldehyde, syringaldehyde, scopoletin, coniferaldehyde, 5-hydroxymethyl-2-furaldehyde
Revilla et al. (1988)	Fino, oloroso and amontillado Sherrys	Myricetin, quercetin, kaempferol and isorhamnetin and quercetin -3- <i>O</i> -rutinoside, quercetin -3- <i>O</i> -glucoside, quercetin -3- <i>O</i> -galactoside, kaempferol -3- <i>O</i> -rutinoside, quercetin -3- <i>O</i> -glucuronoside, quercetin -3- <i>O</i> -rhamnoside, myricetin -3- <i>O</i> -rhamnoside
Cartoni et al. (1991)	Italian wines, <sup>a</sup> fino sherry	Gallic, vanillic, syringic, caffeic, <i>p</i> -hydroxybenzoic, <i>p</i> -coumaric, <i>m</i> -coumaric and ferulic acids
Barón et al. (1997)	Sherry type wine	Gallic, protocatechuic, vanillic, syringic, caffeic, <i>p</i> -coumaric, <i>trans</i> -caffeoyltartaric, <i>cis</i> - coumaroyltartaric, <i>trans</i> -coumaroyltartaric, feruloyltartaric and ferulic acids, catechin, epicatechin, tyrosol, procyanidin B1, procyanidin B2, procyanidin B3, procyanidin B4
	<i>Table wines</i>	
Salagoity-Auguste and Bertrand (1984)	Red Bordeaux wines	Gallic, protocatechuic, vanillic, syringic, caffeic, <i>p</i> -hydroxybenzoic, <i>p</i> -coumaric and ferulic acids, tyrosol, tryptophol, catechin, epicatechin, procyanidin A2, procyanidin B2, procyanidin B3, procyanidin B4, myricetin, quercetin
Puech (1987)	Bulgarian Cabernet Sauvignon and Merlot wines	Vanillin, syringaldehyde
Lunte et al. (1988)	Burgundy wine (USA)	Catechin, epicatechin, procyanidin B2
Wilker and Gallander (1988)	Seyval blanc wine	Gallic, protocatechuic, vanillic, syringic, <i>p</i> -coumaric and ferulic acids
Moutounet et al. (1989)	Chardonnay wine	Gallic, caffeic, <i>p</i> -coumaric, <i>cis</i> - caffeoyltartaric, <i>trans</i> - caffeoyltartaric, 2- <i>S</i> - caffeoyltartaric glutathionyl, <i>cis</i> - coumaroyltartaric, <i>trans</i> - coumaroyltartaric, <i>p</i> -hydroxybenzoic, ferulic, feruloy tartaric and ellagic acids, vanillin, syringaldehyde, coniferaldehyde, Vescalin, castalin, castalagin, procyanidin B1, 5-hydroxymethyl-2-furaldehyde, 2-furaldehyde, tyrosol, tryptophol, lyoniresinol, ethyl caffeate, ethyl <i>p</i> -coumarate
Roggero and Archier (1989)	Côte du Rhône, Daumas-Gassac, Vosne-Romanée wines	Gallic, protocatechuic, <i>p</i> -hydroxybenzoic, vanillic, syringic, caffeic, <i>p</i> -coumaric, caffeoyltartaric and coumaroyl tartaric acids, catechin, epicatechin, tyrosol
Woodring et al. (1990)	Vidal Blanc wine	Gallic, caffeic, <i>p</i> -hydroxybenzoic, <i>m</i> -hydroxybenzoic <i>p</i> -coumaric, salicylic, 3,4-dihydroxyphenylacetic and ferulic acids
Archier et al. (1993)	Carignan, Syrah, Grenache, Mourvèdre, Caberet Franc and Cabernet Sauvignon wines	Gallic, protocatechuic, <i>p</i> -hydroxybenzoic, vanillic, syringic, caffeic, <i>p</i> -coumaric caffeoyltartaric, 2- <i>S</i> - caffeoyltartaric glutathionyl and coumaroyl tartaric acids, catechin, epicatechin, tyrosol, tryptophol, procyanidin B1, procyanidin B2, ethyl caffeate, ethyl <i>p</i> -coumarate, rutin, myricetin, quercetin
Lamuela-Raventos and Waterhouse (1994)	Cabernet Sauvignon and Merlot wines	Gallic, <i>cis</i> - caffeoyltartaric, <i>trans</i> - caffeoyltartaric, 2- <i>S</i> - caffeoyltartaric glutathionyl, <i>cis</i> - coumaroyltartaric, procyanidin B1, procyanidin B2, catechin, epicatechin, rutin, delphinidin-3-glucoside, petunidin-3-glucoside, cyanidin-3-glucoside, malvidin-3-glucoside, peonidin-3-glucoside, delphinidin-3-glucoside-acetate, petunidin-3-glucoside-acetate, cyanidin-3-glucoside-acetate, malvidin-3-glucoside-acetate, peonidin-3-glucoside-acetate, malvidin-3-glucoside- <i>p</i> -coumarate, peonidin-3-glucoside- <i>p</i> -coumarate
Laszlavik et al. (1995)	Red Hungarian wines	Gallic, protocatechuic, vanillic, syringic, caffeic, <i>p</i> -coumaric and ellagic acids, and vanillin, syringaldehyde, 5-hydroxymethyl-2-furaldehyde and 5-methyl-2-furaldehyde
Goldberg et al. (1996)	Commercial table wines from Italy, France, Australia, USA	Catechin, epicatechin, rutin, quercetin, <i>cis</i> -polydatin, <i>cis</i> -resveratrol, <i>trans</i> -polydatin, <i>trans</i> -resveratrol

<sup>a</sup> Not fortified wines.

### 3. Results and discussion

#### 3.1. Method development

The presented method was developed initially for the separation, identification and quantification of wood derived phenolic compounds, such as vanillin, syringaldehyde, vanillic acid and syringic acid, in fortified wines. It was based on a preparative HPLC method for the separation of wood derived phenolic compounds from an extract of oak wood (Puech et al., 1988). Initial results using this method showed many overlapping peaks with poor separation between compounds, such as vanillin and syringic acid. The optimisation of the separation of these compounds was achieved after experimenting with various gradient profiles, mobile phase flowrates and also different mobile phases, such as acetonitrile. During this period, it became apparent that the method could also be used for the separation of other phenolic compounds and also furans that were present in these wood-aged wines. These included resorcinol, an extractive of *Quercus rubra* (Seikel et al., 1971), and maltol, one of the most important carbohydrate degradation compounds derived from oak wood

(Sefton, 1991) and commonly associated with 5-hydroxymethyl-2-furaldehyde through the maillard reaction pathway. Up to 28 standard compounds could be separated and identified in a 20% ethanol–water mixture according to the criteria shown in Table 2. These included classes of phenolic compounds, such as hydroxybenzoic acids, hydroxycinnamic acids, phenolic aldehydes, coumarins, flavan-3-ols and flavonol aglycones, some of which are found only in wood-aged wines and spirits, and other compounds involved in browning reactions in food systems (furans and pyranones).

#### 3.2. Identification and quantification of phenolic compounds

Fig. 1 shows the chromatographic profiles of phenolic compounds and furans in 5 different types of fortified wines and a naturally sweet wine. Thirteen phenolic compounds were identified (Table 3), 7 of which have been shown to be present in natural and toasted wood extracts (Laszlavik et al., 1995). The limit of detection and limit of quantification of these compounds, calculated as  $3\sigma$  and  $10\sigma$  above the peak to peak noise level (Analytical Chemistry, 1980), were very low (Table 4).

Table 2  
Retention times and spectra characteristics of standard compounds investigated

Compound no.	Name	Retention time, Rt (min) mean <sup>a</sup> ± SD	RSD (%) <sup>b</sup>	Spectral $\lambda_{\max}(1)$	characteristics $\lambda_{\max}(2)$
1	Gallic acid	9.17 ± 0.17	1.80	270	—
2	Resorcinol	10.61 ± 0.07	0.65	273	—
3	5-Hydroxymethyl-2-furaldehyde (HMF)	13.33 ± 0.03	0.26	283	—
4	Protocatechuic acid	14.59 ± 0.07	0.50	293	258
5	Furfural	16.80 ± 0.06	0.33	276	—
6	<i>p</i> -Hydroxybenzoic acid	21.22 ± 0.12	0.59	252	—
7	Gentisic acid	22.10 ± 0.25	1.12	328	—
8	Maltol	22.58 ± 0.12	0.54	274	—
9	<i>p</i> -Hydroxybenzaldehyde	26.16 ± 0.20	0.78	283	—
10	Esculin	26.78 ± 0.52	1.93	332	294
11	(+)-Catechin	27.62 ± 0.45	1.65	276	—
12	Vanillic acid	29.99 ± 0.09	0.30	290	258
13	5-Methylfurfural	30.06 ± 0.27	0.89	291	—
14	Esculetin	32.51 ± 0.27	0.84	344	296
15	Caffeic acid	33.72 ± 0.26	0.76	322	294
16	Chlorogenic acid	35.94 ± 0.22	0.61	324	298
17	Vanillin	37.18 ± 0.30	0.81	308	278
18	Syringic acid	38.44 ± 0.24	0.62	274	—
19	(–)-Epicatechin	42.56 ± 0.24	0.56	276	—
20	<i>p</i> -Coumaric acid	45.39 ± 0.08	0.17	310	—
21	Syringaldehyde	45.51 ± 0.04	0.09	306	—
22	Salicylic acid	48.06 ± 0.17	0.35	300	—
23	Ferulic acid	53.55 ± 0.31	0.59	342	296
24	Scopoletin	53.70 ± 0.62	1.16	322	296
25	Coniferaldehyde	57.77 ± 0.39	0.68	338	302
26	Ellagic acid	80.18 ± 0.12	0.15	366	290
27	Myricetin	80.35 ± 0.40	0.50	370	266
28	Quercetin	89.07 ± 0.10	0.11	370	266

<sup>a</sup> Mean of retention times ± standard deviations for 4 replicates.

<sup>b</sup> Relative standard deviations of retention times (%).

In most cases the older wines of the same type, the Colheita ports, Aged Tawny ports and the tokay wines, had a higher concentration of total identified phenolic compounds. As a group of wines, the tawny ports had more wood derived phenolic compounds than all the

others. Ellagic acid and vanillin, tentatively identified by comparison to the retention time of standards, were found only in these wines. Vanillic acid, syringic acid, protocatechuic acid and ellagic acid were present in higher concentrations in the older wines of the two styles

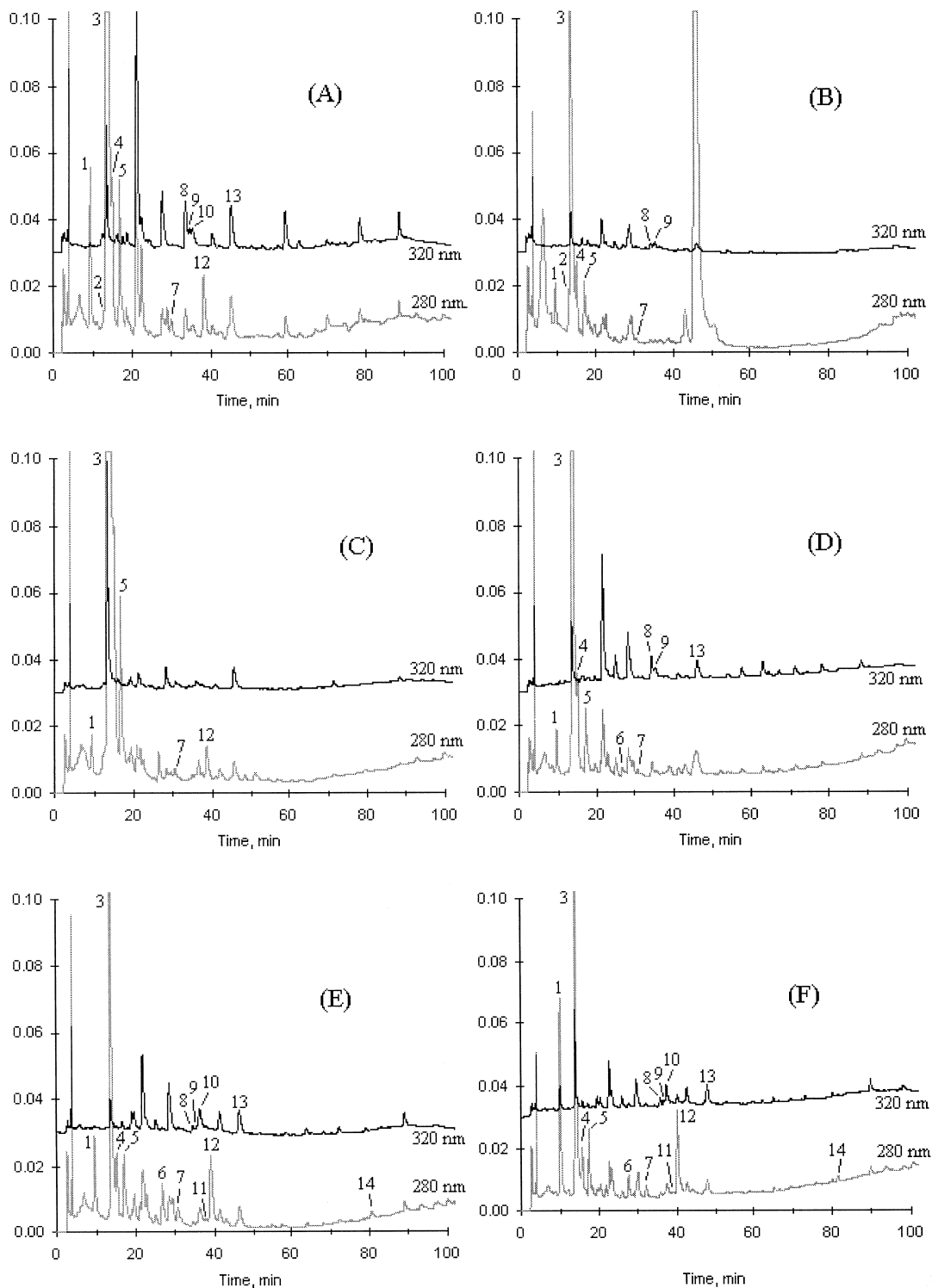


Fig. 1. Chromatographic profiles of phenolic compounds and furans in different fortified wines. (A), Banyuls 1977; (B), Tokay 1983; (C), 10 years old Madeira; (D), Amontillado sherry; (E), Tawny port Colheita 1960; (F), 10 years old Tawny port. Peak numbers are identified in Table 3.

Table 3  
Concentration of phenolic compounds and furans identified in various fortified wines (mg l<sup>-1</sup>)

Peak no.	Wines	Port 10 years	Port 30 years	Port 1990	Port 1960	Sherry	Madeira 10 years	Tokay 1988	Tokay 1983	Banyuls 1989	Banyuls 1977
1	Gallic acid	27.0	30.5	13.6	12.1	5.2	5.3	4.0	5.3	32.8	22.3
2	Resorcinol <sup>a</sup>	—	—	—	—	—	—	1.9	2.1	tr	tr
3	5-Hydroxymethyl-2-furaldehyde	33.2	168.7	tr	35.5	86.8	361.0	19.5	42.9	tr	162.4
4	Protocatechuic acid	13.9	20.2	3.0	9.2	7.2	—	4.3	7.7	5.1	13.5
5	Furfural	3.5	7.8	0.8	3.8	2.9	8.8	0.8	1.8	—	8.7
6	<i>p</i> -Hydroxybenzaldehyde	tr	0.6	tr	0.9	tr	—	—	—	tr	—
7	Vanillic acid	3.0	4.6	4.5	5.6	1.5	3.6	1.3	1.2	4.5	5.0
8	Caffeic acid	1.2	1.5	1.4	1.1	2.3	—	1.1	0.9	3.9	4.6
9	Chlorogenic acid isomer <sup>a</sup>	1.1	0.8	2.4	1.0	2.1	—	2.3	2.0	2.8	1.8
10	Chlorogenic acid	5.1	4.4	12.8	6.1	—	—	—	—	2.0	3.0
11	Vanillin <sup>a</sup>	tr	0.4	—	0.2	—	—	—	—	—	—
12	Syringic acid	8.6	10.6	8.0	8.6	—	4.2	—	—	7.6	8.2
13	<i>p</i> -Coumaric acid	2.7	3.0	3.3	4.2	3.4	—	—	—	6.5	6.5
14	Ellagic acid	2.4	3.1	3.3	3.7	—	—	—	—	—	—
15	Myricetin	—	—	—	—	—	—	—	—	4.5	—
	Total phenolic compounds	65	79.7	52.3	52.7	21.7	21.9	14.9	19.2	69.7	64.9
	Total furans	36.7	176.5	0.8	39.3	89.7	369.8	20.3	44.7	tr	171.1

tr, trace amounts below the limit of quantification (LOQ); —, not detected, below the limit of detection (LOD).

<sup>a</sup> Tentatively identified.

Table 4  
Detection limits of identified phenolic compounds and furans

Compound	Limit of detection (LOD) (μg l <sup>-1</sup> )	Limit of quantification (LOQ) (μg l <sup>-1</sup> )
Gallic acid	1.95	4.87
Resorcinol	0.54	1.36
5-Hydroxymethyl-2-furaldehyde	5.66	14.15
Protocatechuic acid	3.25	8.13
Furfural	0.74	1.85
<i>p</i> -Hydroxybenzaldehyde	5.50	13.76
Vanillic acid	1.13	2.83
Caffeic acid	3.41	8.54
Chlorogenic acid	1.49	3.74
Vanillin	4.53	11.32
Syringic acid	3.85	9.62
<i>p</i> -Coumaric acid	3.74	9.36
Ellagic acid	0.75	1.88
Myricetin	9.84	24.61

of tawny ports examined. Gallic acid was in much higher concentrations in Aged Tawny ports than the Tawny Colheita ports. The presence of higher concentrations of these phenolic compounds in the older wines may have been the result of their extraction from wood during ageing. However, a previous study demonstrated that phenolic compounds, such as gallic acid, syringic acid, vanillic acid and protocatechuic acid, can increase in table wine aged in bottle for nine months as the result of the degradation of tannins (Archier et al., 1993). It is likely that some of the differences in the concentration of phenolic compounds were caused by both wood extraction and the degradation of tannins.

*p*-Hydroxybenzaldehyde was found in trace quantities in the Banyuls 1989, the Amontillado sherry and in all of the tawny ports. Myricetin was found only in the Banyuls Rimage 1989 and a compound eluting very closely to HMF in both Tokay and Banyuls wines, was tentatively identified as resorcinol, an extractive of *Quercus rubra* (Seikel et al., 1971). To the best of our knowledge, this is the first time resorcinol has been identified in wood-aged wines. The identification was based on the spectral characteristics and retention time of a commercial standard. Peak 9 was tentatively identified as a chlorogenic isomer as it had identical spectral characteristics to chlorogenic acid. Isomers of chlorogenic acid have been identified previously in apple juice and in tobacco (Court, 1977; Spanos et al., 1990).

Many phenolic compounds, including some coumarins and phenolic aldehydes (Table 1), which have been found in wood-aged table wines (Achilli et al., 1993) and sherry (Estrella et al., 1986), were not found in the wines analysed. Coumarins, such as scopoletin, has been found at a concentration of 15.5 μg l<sup>-1</sup> in a diethyl ether extract from a red wine aged in new wood using fluorescence detection (Salagoity-Auguste et al., 1987). Their presence as trace quantities in wines would have made them undetectable by the UV method that had been developed.

Oxidation of phenolic compounds, such as syringaldehyde and vanillin, to their corresponding acids (Puech, 1981), or the oxidation of caffeic acid under acidic condition to tetrahydrofuran derivatives (Fulcrand et al., 1994), may limit their presence in the wines analysed. Certain hydroxycinnamic acids like ferulic acid can also be converted to 4-vinylguaiacol by yeast

when a wine is aged in old barrels (Chatonnet et al., 1992), which may explain its absence in the wines analysed.

### 3.3. Identification and quantification of furans

5-Hydroxymethyl-2-furaldehyde (HMF) and furfural were identified in all of the wines analysed, although furfural was not found in the Banyuls Rimage 1989. The younger wines had lower amounts of both furans than the older wines indicating the importance of these compounds in the ageing process. Furfural has been known to increase during the bottle ageing of Riesling wines (Simpson, 1980) and in wood-aged Italian wines (Stefano, 1988). The amounts of furfural found in this study ranged from as low as  $0.8 \text{ mg l}^{-1}$  in the tawny colheita port 1990 to  $8.8 \text{ mg l}^{-1}$  in the 10 years old Verdelho madeira.

HMF in tawny ports was on average much higher than previously found in tawny port wines by Williams et al. (1983). The 10 years old Verdelho madeira had the highest concentration of HMF probably not so much as the result of wood ageing, but mainly from the Estufagem process, which is a three month maturation period at around  $41^\circ\text{C}$  (Goswell et al., 1977). The concentrations of HMF and furfural found in the Amontillado sherry, although slightly higher, were very close to the ones found previously by gas chromatography (Shimizu and Watanabe, 1979). 5-methylfurfural which has been identified in Australian tawny port wines (Simpson, 1980) and Tokay Aszú wines (Schreier et al., 1976) by gas chromatography was not identified in the wines analysed in this study.

## 4. Conclusions

HPLC with diode array detection has shown the presence of a number of wood derived phenolic compounds and furans in a range of different dessert wines. Phenolic composition varied in terms of class, number and the concentration of individual compounds identified. The presence of higher concentrations of total phenolic compounds and furans in older wines, as in the case of the tawny ports, suggests that wood ageing plays an important role in the evolution of these compounds. However, the degree of importance of the role of oxidation, interaction and degradation of these compounds with time, and the extraction of these compounds from wood in the ageing of fortified wines needs to be studied further.

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